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FUEL CELL ELECTRODE-ELECTROLYTE UNIT
[Elektroden-Elektrolyt-Einheit fuer eine Brennstoffzelle]

Hendrik Dohle, et al.

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INVENTORS	(72):	DOHLE, HENDRIK; PEINECKE, VOLKER; BUSENBENDER, ILONA; KELS, THORSTEN
APPLICANT	(71):	FORSCHUNGSZENTRUM JUELICH GMBH
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The invention relates to an electrode-electrolyte unit for a fuel cell consisting of a proton-conductive electrolyte which on one side is provided with a catalytically active anode and on the opposite side with a catalytically active cathode, and which works with a fuel from which protons are split off on the anode. The fuel can be for example hydrogen or methanol. Membranes or other solid electrolytes, consisting for example of a ceramic, or liquid electrolytes are possible as the electrolytes.

Fuel cells are systems which convert chemical into electrical energy. The central electrochemical function element of a fuel cell is the electrode-electrolyte unit. Such an electrode-electrolyte unit with a ceramic solid electrolyte is known for example from DE 40 33 286 A1. Other proton-conductive solid electrolytes in the form of oxides or fluorides are suggested in DE 39 29 730 C2 = EP 0 417 464 A1.

Membrane fuel cells have an ion-conductive membrane which is located between two catalytically active electrodes, the anode and the cathode. The membrane is for example a polymer material. The anode material is preferably platinum or a platinum-ruthenium alloy, the cathode material is platinum. The anode and cathode material is either deposited wet-chemically on the membrane or it is present in powder form and is hot-pressed to the membrane.

DE-PS 42 41 150 describes processes according to which these membrane electrode units can be produced.

In a fuel cell which, as initially indicated, is operated directly with methanol, so-called direct methanol fuel cells, or with

* Numbers in the margin indicate pagination in the foreign text.

another fuel from which protons are split off on the anode of the membrane-electrode unit, the protons penetrate the electrolyte layer and react on the cathode side with the oxygen which has been supplied there, with the formation of water. Fuel cells which are operated with hydrogen work analogously.

One disadvantage of the known fuel cells is that not only ions can pass through the electrolyte, but in part also the hydrate sheaths of the hydrogen ions or some of the fuel. For methanol-operated fuel cells methanol molecules are allowed to pass by the electrolyte.

The disadvantage is that the methanol on the one hand poisons the cathode, which leads to reduced cell voltage, and on the other hand the oxidizable portion of the methanol on the anode is reduced, by which the degree of fuel utilization of the fuel cell is reduced.

For hydrogen fuel cells water entrainment causes the anode to dry out; this leads to a decrease of power. It is therefore necessary to additionally humidify the hydrogen.

Existing approaches to a solution of the problem of methanol diffusion in direct methanol fuel cells consist in part in completely reacting the methanol on the anode by improving anode kinetics, for example by the corresponding activity of the anode, so that a low methanol concentration is established on the anode/ electrolyte phase boundary. In this way the amount of methanol which penetrates into the electrolyte layer and which passes through it will be reduced. But to date no anode structures have become known which could adequately prevent the diffusion of methanol in all operating states.

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The object of the invention is to devise an electrode-electrolyte unit of the initially named type in which the penetration of the fuel

used or the penetration of water through the electrolyte layer is prevented.

As claimed in the invention, the object is achieved in that the electrolyte is divided into two electrolyte layers between which there is a single-ply or multi-ply blocking layer of a pore-free or closed-pore material which is impermeable to all other substances and which accepts protons on one side and releases protons on the opposite side.

Depending on the requirements, the electrolyte layers can be of equal or different thickness and can be produced from the same, for example polymer, materials or from different types of material.

The blocking layer is especially impermeable to methanol and water. A suitable blocking layer material has been a palladium-silver alloy.

The silver portion in the alloy is preferably at least 25% by weight. The hydrogen ions (protons) can more or less diffuse through this blocking layer with low resistance by their recombining on one side to form hydrogen which then penetrates the blocking layer and is again dissociated on the opposite side, while other substances with large molecule sizes, here especially water and methanol, are retained. The released electrons migrate back to the side which accepts protons.

The blocking layer is preferably a film with a thickness of 5-50 /4 microns.

One advantageous configuration of the invention consists in coating the blocking layer on both sides with a catalytically active, porous layer with a more highly active surface.

The porous layer on the side facing the anode thus has the function that a sufficient amount of hydrogen is dissolved while the

porous layer on the side facing the cathode causes the electrochemically active surface to be enlarged.

This porous layer or these porous layers can be applied in the known manner, for example by electrochemical deposition, or they are present in the form of a powder which is applied to the blocking layer. In turn, a palladium-silver alloy, platinum, a platinum-ruthenium alloy or one or more elements of main group VIII of the periodic system or their alloys can be the material for the porous layer.

The blocking layer combination is then joined to the other elements of the electrode-electrolyte unit in the already known manner, as is described for example for membrane-electrode units in several versions in the aforementioned document.

Another advantageous configuration of the electrode-electrolyte unit as claimed in the invention, especially for membrane fuel cells and here especially for hydrogen-oxygen fuel cells, consists in that the blocking layer is made so thick that it contributes significantly to the mechanical stability of the electrode-electrolyte unit. Favorable values are 10-50 microns. This allows the bordering polymer layers to be kept very thin (5-20 microns), by which their proton conductivity is promoted. Without the blocking layer especially for thin polymer membranes there is the problem that oxygen can diffuse from the cathode to the anode, by which the power of the fuel cell is reduced.

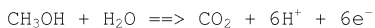
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The invention will be detailed below using one embodiment of the membrane fuel cell. In the pertinent drawings

Figure 1 shows the schematic structure of a membrane fuel cell and Figure 2 shows a diagram for the processes on and in the blocking

layer of the membrane-electrode unit.

The electrode-electrolyte unit as claimed in the invention, here a membrane-electrode unit 1, as is shown in Figure 1, borders the anode space 2 to which a methanol-water mixture as fuel is supplied. The methanol reaches the anode 3 on which by the following anode reaction



hydrogen ions (protons), electrons and carbon dioxide are formed. The electrons are released on the anode by a current distributor which is not shown here in an external (consumer) circuit and are supplied to the cathode. The hydrogen ions penetrate a following electrolyte layer which consists of a polymer membrane 4, here methanol and water being entrained at the same time. Methanol and water are retained by a following blocking layer 5 of a palladium-silver alloy as claimed in the invention, while the protons can more or less diffuse (see the aforementioned manner of operation or the one detailed below).

The blocking layer 5 is followed by a conventional polymer /6
membrane 6 through which the hydrogen ions travel to the cathode 7 on which they react with oxygen which is supplied to the cathode 7 in the cathode space 8.

The membrane-electrode unit 1 is produced as follows:

A rough and microporous palladium-silver structure with a layer thickness of roughly 3 microns is applied to a thin palladium-silver foil (roughly 5 microns) on either side by electrochemical deposition. These porous layers 5a, 5b are indicated in Figure 2 on either side of the blocking layer 5. The porous structure is desirable in order to have a large surface and to create a region which conducts both electrons and also ions for the two required electrochemical reactions.

The intermediate layer which has been formed in this way is now coated on both sides with an ion-conductive polymer. For this purpose, a solution of the polymer in a water-alcohol mixture is slowly sprayed onto a porous layer with a spray gun at a uniform distribution. The spray gas is nitrogen here. The polymer layer provides for intensive joining of the ion-conducting polymer to the surface of the intermediate layer by its filling the porous intermediate spaces on the surface of the porous layer. After drying, the other side of the intermediate layer is treated in the same manner.

The blocking layer-polymer combination which has been formed in this way (roughly 10-15 microns thick) is connected after drying of the second side with two polymer membranes 4 and 6 by means of a hot pressing process to the membrane as claimed in the invention. To do this, the combination is inserted between two polymer membranes 4 and 6 (each roughly 50 microns thick) and by applying pressure and temperature is pressed to them. Favorable process parameters are a pressure of 200 bars, a temperature of 130°C and a pressing time of 10 minutes. /7

This membrane which is provided with a blocking layer can now be used in a conventional membrane-electrode unit by its being provided with a cathode in a similar manner.

The action mechanism of the blocking layer can be understood as follows, as is explained below using Figure 2;

On the side facing the anode 3, the hydrogen ions $2H^+$ (protons) which come from the anode 3 on the surface of the blocking layer 5, especially in the upper porous layer 5a, recombine again to form hydrogen H_2 (reduction) which diffuses through the palladium-silver

foil. On the opposite surface (porous layer 5b) it is dissociated upon emergence again into hydrogen ions 2H^+ (oxidation), the free electrodes [sic] of the blocking layer combination which have been captured on the anode side being released again. The released electrons 2e^- migrate through the metallic blocking layer 5 again to the anode side.

In simplified terms the added intermediate layer can be regarded as an electrochemical auxiliary system in which between an auxiliary cathode (porous layer 5a - reduction of hydrogen ions) and an auxiliary anode (porous layer 5b - oxidation of hydrogen) both mass transport and also electron transport which proceeds in the opposite direction take place.

This principle ensures that the hydrogen ions can reach the fuel cells-cathode.

1. Electrode-electrolyte unit for a fuel cell consisting of a proton-conductive electrolyte which on one side is provided with a catalytically active anode (3) and on the opposite side with a catalytically active cathode (7), and which works with a fuel from which protons are split off on the anode (3), characterized in that the electrolyte is divided into two electrolyte layers (4, 6) between which there is a single-ply or multi-ply blocking layer (5) of a pore-free or closed-pore material which is impermeable to all other substances and which accepts protons on one side and releases protons on the opposite side.

2. Electrode-electrolyte unit as claimed in Claim 1, wherein the blocking layer (5) consists of a palladium-silver alloy.

3. Electrode-electrolyte unit as claimed in Claim 2, wherein the silver portion in the alloy is at least 25% by weight.

4. Electrode-electrolyte unit as claimed in one of the preceding claims, wherein the blocking layer (5) is a foil.

5. Electrode-electrolyte unit as claimed in Claim 4, wherein the foil has a thickness of 5-50 microns.

6. Electrode-electrolyte unit as claimed in one of the preceding claims, wherein the blocking layer (5) on both sides is coated with a catalytically active porous layer (5a, 5b) with a more highly active surface.

7. Electrode-electrolyte unit as claimed in Claim 6, wherein the porous layer (5a, 5b) is applied by electrochemical deposition.

8. Electrode-electrolyte unit as claimed in claim 6, wherein the porous layer (5a, 5b) is present in the form of a powder which has been

applied to the blocking layer (5).

9. Electrode-electrolyte unit as claimed in one of Claims 6 to 8, wherein the porous layer (5a, 5b) has a thickness of 1-20 microns.

10. Electrode-electrolyte unit as claimed in one of Claims 6 to 9, wherein the porous layer (5a, 5b) consists of a palladium-silver alloy.

11. Electrode-electrolyte unit as claimed in one of Claims 6 to 9, wherein the porous layer (5a, 5b) consists of platinum.

12. Electrode-electrolyte unit as claimed in one of Claims 6 to 9, wherein the porous layer (5a, 5b) consists of a platinum-ruthenium alloy.

13. Electrode-electrolyte unit as claimed in one of Claims 6 to 9, wherein the porous layer (5a, 5b) consists of one or more elements of main group VIII of the periodic chart or their alloys.

Fig.1

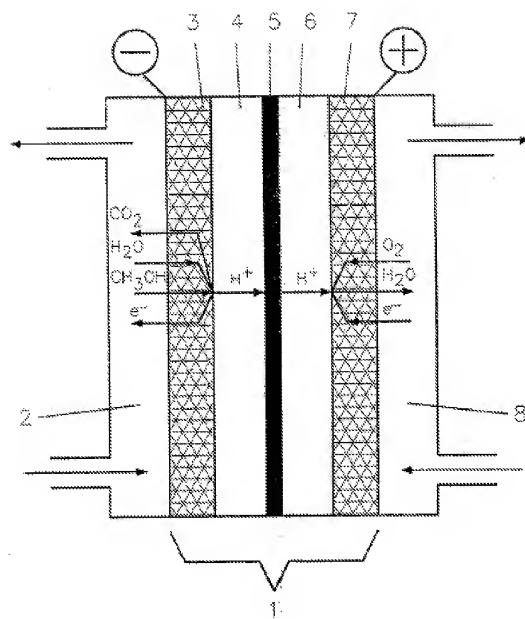


Fig. 2

